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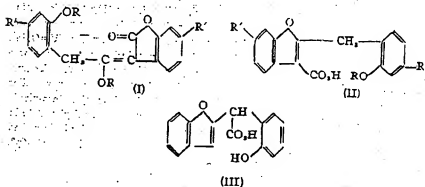
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EXPERIMENTS ON THE SYNTHESIS OF FURANO COMPOUNDS. PART XII. FURTHER TRANSFORMATIONS OF *iso*COUMARANONE

By J. N. CHATTERJEA

The self-condensation product of *isocoumaranone* has been converted into *8-braun*. The constitutions of acid-catalysed transformation products of 3-acyl-*isocoumaranones* have been elucidated. The self-condensation of 6-methoxy-*isocoumaranone* has also been studied.

In Part VI of this series of papers (this *Journal*, 1956, 33, 175), it has been shown that *isocoumaranone* undergoes self-condensation in presence of sodium hydride, yielding 3-*o*-hydroxyphenylacetyl-*isocoumaranone-2* which exists largely in the enolic form (I: R=R'=H). When this compound was boiled with hydrochloric acid in acetic acid, an isomeric phenolic acid was formed in excellent yield which was formulated as either (II: R=R'=H) or (III).

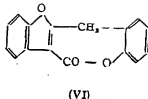
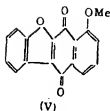
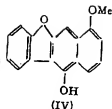


The ambiguity has now been cleared and the isomeric acid has been shown to have the structure (II: R=R'=H) on the following grounds:

(i) The dimethyl ether (I: R=Me; R'=Et) obtained by the action of diazomethane on the self-condensation product gave, on acid treatment, a methoxy-carboxylic acid, identical with the product obtained on methylation of the above mentioned isomeric phenolic acid. From this, it is clear that the phenolic hydroxy group of (I: R=R'=H) did not take part in this transformation, and thus excluding the structure (III) for the isomeric acid.

(ii) The acid chloride derived from the above mentioned methoxy-carboxylic acid gave, on treatment with aluminium chloride, a naphthol, recognised by typical colour reaction with chloroform and alkali (Perkin and Robinson, *J. Chem. Soc.*, 1909, 96, 383).

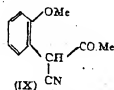
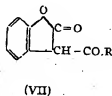
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It is clear therefore that the acid and the naphthol have respectively the structures (II: R=Me; R'=H) and (IV). Further, this α-naphthol on oxidation with chromic acid furnished 7-methoxy-β-brazaquinone (V) which afforded a small quantity of β-braza on vigorous treatment with hydriodic acid, and thus providing an example of unique formation of β-braza from isocoumaranone†. In agreement, 7-methoxy-β-braza also afforded a small amount of β-braza on similar treatment.

The phenolic acid (II: R=R'=H) affords a lactone on treatment with propionic anhydride. This compound, now prepared with thionyl chloride, has undoubtedly the structure (VI). An attempt to prepare this lactone or (II: R=R'=H) by the Wolff-Kishner reduction of the related ketone (VI: CO in place of CH₂; this *Journal*, 1955, 32, 265) resulted in the exclusive formation of the corresponding azine.

It may be noted that in the formation of the acid (II: R=R'=H) from (I: R=R'=H), the furan ring is broken down and then reconstituted. This interesting transformation is found to be general. Thus, the self-condensation product of 6-methoxyisocoumaranone was isomerised by hydrochloric acid in acetic acid to (II: R=H; R'=OMe). Again, 3-acetyl coumaranone-2 (VII: R=Me) (or its acetyl derivative) which was originally regarded by Pfeiffer and Euders (*Chem. Ber.*, 1951, 84, 247) as 2-methylcoumarone-3-carboxylic acid (VIII: R=Me) was, indeed, converted into the latter in a similar way. The constitution of the acid was settled by its synthesis* from the keto-nitrile (IX), obtained from o-methoxyphenylacetonitrile by condensation with ethyl acetate in presence of sodium hydride. On treatment with hydrobromic acid, this nitrile furnished a mixture of the acid (VIII: R=Me), 2-methylcoumarone and a product of m.p. 158-60°, probably a polymeride of 2-methylcoumarone.

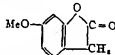


In a like manner, 3-propionylcoumaranone-2 and 6-methoxy-3-acetyl coumaranone-2 were isomerised to 2-ethylcoumarone-3-carboxylic acid and 6-methoxy-2-methylcoumarone-3-carboxylic acid respectively. 3-Benzoylcoumaranone-2, however, afforded 2-phenylcoumarone.

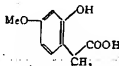
† An account was published in *Exper.*, 1956, 12, 37.

* The acid has also been synthesized recently by Goldmann and Aronov [*J. Amer. Chem. Soc.*, 1955, 77, 1563] who have worked on a related but significantly different topic.

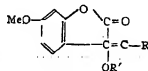
6-Methoxyisocoumaranone (X) (Hromatka, *Ber.*, 1942, 75, 123) has now been conveniently prepared from 2-hydroxy-4-methoxybenzaldehyde by alactonisation (Robertson, *J. Chem. Soc.*, 1933, 493), hydrolysis by baryta to 2-hydroxy-4-methoxyphenylpyruvic acid, followed by oxidation with hydrogen peroxide to the acetic acid (XI), and then cyclisation by distillation. 6-Methoxycoumaranone-2 proved chemically similar to isocoumaranone itself, except that its reactivity was less pronounced. The compound was acylated by acetic anhydride and sodium acetate to (XII: R=Me; R'=COMe); by propionic anhydride and sodium propionate to (XII: R=Et; R'=COEt) and by benzoic anhydride and sodium benzoate to 6-methoxy-3-benzoylcoumaranone-2 (XII; R=Ph; R'=H). The self-condensation of 6-methoxycoumaranone-2 was brought about with sodium hydride yielding (I: R=H; R'=OMe). The infra-red spectrum of this compound is consistent with this structure. This compound underwent rearrangement in quantitative yield to (XII: R'=Me; R'=COMe) with acetic anhydride and sodium acetate (cf. Part VI, *loc. cit.*). As expected, the ultraviolet absorption curves of the acyl derivatives (XII: R=Me; R'=H), (XII, R=Ph; R'=H) and (I, R=H; R'=OMe) were similar.



(X)



(XI)



(XII)

* EXPERIMENTAL *

Enolic Methyl Ether of 3-O-Methoxyphenylacetyl coumaranone-2 (I: R=Me; R'=H).—Excess of diazomethane (ca. 4M) was added to an ethereal suspension of the self-condensation product of isocoumaranone (1M) and the reaction mixture left in the cold overnight. The sticky mass left on removal of the solvent furnished a crystalline product (yield, 30-35%) on trituration with methanol. The compound was washed with dilute alkali and crystallised from methanol in colorless crystalline mass, m.p. 104°, exhibiting a negative ferric reaction. (Found: C, 73.6; H, 5.6. $C_{14}H_{10}O_4$ requires C, 73.0; H, 5.4%).

2-O-Methoxybenzyl coumaranone-3-carboxylic Acid.—A solution of the foregoing enolic ether (0.6 g.) in acetic acid (3 c.c.) was boiled with HCl (conc., 1 c.c.) for 3 hours and the product precipitated with water. The greenish semi-solid mass was dried, dissolved in benzene-petroleum ether and the solution allowed to evaporate spontaneously in a refrigerator, when apparently two types of crystals were obtained which were easily separated: (a) greenish prisms, m.p. 145° and (b) colorless prisms, m.p. 154°; mixed m.p. of both the samples was 145-54°, indicating that the sample, m.p. 154°, was purer. This on recrystallisation from acetic acid was obtained in colorless prisms, m.p. 157°, giving a negative ferric reaction. (Found: C, 72.1; H, 4.9. $C_{14}H_{10}O_4$ requires C, 72.3; H, 5.0%). The compound imparted a violet colour to sulphuric acid.

* All m.p.'s are uncorrected

Methylation of (II: R=R'=H).—If the acid is methylated in sodium carbonate solution with methyl sulphate, the product obtained in good yield is methyl 2-*o*-hydroxybenzylcoumarone-3-carboxylate, m.p. 130°, underpressed on admixture with an authentic specimen. (Found: C, 72.2; H, 5.0. Calc. for $C_{17}H_{14}O_4$: C, 72.3; H, 5.0%). When the methylation is done with excess of methyl sulphate and alkali on the water-bath, the alkaline layer filtered and acidified, 2-*o*-methoxybenzylcoumarone-3-carboxylic acid was obtained (58% yield), crystallising from acetic acid in colorless prisms, m.p. 157.5°, underpressed on admixture with the sample obtained above. (Found: C, 72.2; H, 5.0. $C_{17}H_{14}O_4$ requires C, 72.3; H, 5.0%). *U. V. absorption*: Continuous absorption in the U. V. region without exhibiting a maxima or minima. *Infra-red spectrum*: λ_{max}^{NaCl} 6.054, 6.259 (COOH), 6.8s (CH₂) and 8.9.0s (ether) μ .

7-Methoxy- β -brazanquinone.—The above acid (0.6 g.) was converted into the acid chloride with thionyl chloride (1.2 c.c.) in CS_2 solution. After removing the solvent, the oily acid chloride was dissolved in CS_2 (12 c.c.) and treated with $AlCl_3$ (0.9 g.) when a yellow aluminium complex separated. The mixture was left overnight, solvent removed by decantation and the residue treated with iced HCl. A semi-solid product (yield > 100%) was obtained which gave a typical Berlin blue colour with sodium hydroxide and chloroform and coupled with diazonium salts to yield azo colours. As the compound was found difficult to purify, the crude material (0.4 g.) in acetic acid (6 c.c.) was oxidised by boiling with chromic acid (0.6 g.) in a small quantity of water. After the exothermic reaction was over (4 min.), the quinone (V) (0.2 g.) was isolated as usual and crystallised from acetic acid in yellow prisms, m.p. 242°. It developed a purple colour with sulphuric acid. (Found: C, 73.1; H, 3.8. $C_{17}H_{14}O_4$ requires C, 73.6; H, 3.6%).

β -Brazan.—The above quinone (0.1 g.) was boiled vigorously with HI (6 c.c.) for 2 hours. The crystalline product that condensed on the walls of the condenser was collected from time to time (2-4 mg.) and was identified by determination of m.p. and mixed m.p. The residue in the flask contained dirty phenolic materials which were not investigated.

7-Methoxy- β -brazan.—A mixture of 7-keto-7:8:9:10-tetrahydro- β -brazan (1.8 g., this *Journal*, 1953, 30, 103), N-bromosuccinimide (0.9 g.) and a few crystals of benzoyl peroxide in chloroform (25 c.c.) was refluxed for 6 hours. The product, worked up in the usual manner, was warmed with pyridine (5 c.c.) for 20 minutes on the water-bath. The mixture was acidified and the crude 7-hydroxy- β -brazan collected and purified by extraction with alkali. The phenol (0.9 g.) was methylated by refluxing in acetone (20 c.c.) with methyl iodide (1 c.c.) and dry potassium carbonate (5 g.) for 6 hours. The methyl ether, obtained in quantitative yield, was purified by sublimation and obtained in pointed blades, m.p. 170°. The compound dissolved in sulphuric acid giving a yellow solution, turning blue and finally green. (Found: C, 82.0; H, 4.9. $C_{17}H_{14}O_4$ requires C, 82.2; H, 4.8%). On vigorous boiling with HI this compound gave a small quantity of β -brazan.

This compound on oxidation with chromic acid in acetic acid in the usual manner afforded a yellow quinone, m.p. 245.46° after purification by sublimation. This compound is presumably 7-methoxy- β -brazanquinone, but the determination of mixed m.p.

with the quinone, m.p. 242° described above, could not be carried out due to the loss of the latter by accident. With H_2SO_4 the compound developed a purple colour.

2-O-Hydroxybenzylcoumarone-3-carboxylic Acid Lactone (VI).—The acid (II: $\text{R}=\text{R}'=\text{H}$) (0.2 g.) was boiled with purified thionyl chloride (2 c.c.) till the crystals went into solution, and then left for 2 hours. Thionyl chloride was removed in vacuum leaving a gum which crystallised on titration with alcohol. The lactone crystallised from alcohol in colorless prisms, m.p. 138° , undepressed on admixture with a specimen prepared with the aid of propionic anhydride. (Found: C, 76.7; H, 4.0. Calc. for $\text{C}_{11}\text{H}_8\text{O}_5$: C, 76.8; H, 4.0%).

Wolff-Kishner Reduction of 2-O-Hydroxybenzylcoumarone-3-carboxylic Acid Lactone.—A mixture of the lactone (0.2 g., this *Journal*, 1955, 32, 265), KOH (0.6 g.) and hydrazine hydrate (1 c.c., 80%) was refluxed for 1½ hours; water was removed from the system by distillation and then the mixture heated at $100-105^{\circ}$ for 3½ hours. The dark solution was diluted with water (charcoal), filtered, acidified and the resulting solid crystallised from acetic acid. The product appeared to be the corresponding azine which was obtained in colorless plates, m.p. $> 300^{\circ}$, exhibiting a yellow coloration with H_2SO_4 . (Found: C, 69.1; H, 3.9. $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_2$ requires C, 68.6; H, 3.6%).

Keto-nitrile (IX).—A mixture of *o*-methoxyphenylacetone nitrile (3.0 g.), sodium hydride (0.95 g.) and ethyl acetate (4 c.c.) in benzene (30 c.c.) was refluxed for 4 hours after the addition of a drop of alcohol. The sodium salt of the keto-nitrile separated. The nitrile (2.9 g.), worked up in the usual manner, was obtained in prisms, m.p. $84-85^{\circ}$ from acetic acid. (Found: C, 70.5; H, 5.8. $\text{C}_{11}\text{H}_8\text{O}_4\text{N}$ requires C, 69.8; H, 5.8%).

2-Methylcoumarone-3-carboxylic Acid.—(a) A mixture of the foregoing keto-nitrile (8.0 g.), acetic acid (60 c.c.) and HBr (50 c.c., 48%) was refluxed for 5 hours. The mixture was cooled, diluted with water and extracted with ether (3×30 c.c.). The ethereal layer was washed with dilute alkali and the alkaline layer acidified to afford the carboxylic acid (0.4 g.) which crystallised from aqueous alcohol in colorless plates, m.p. $191-91.5^{\circ}$ (lit., m.p. 191°). (Found: C, 68.0; H, 4.6. Calc. for $\text{C}_{11}\text{H}_8\text{O}_5$: C, 68.2; H, 4.5%). The amide crystallised from alcohol in colorless needles, m.p. 179° , showing no coloration with H_2SO_4 . (Found: C, 68.2; H, 4.7. $\text{C}_{11}\text{H}_8\text{O}_4\text{N}$ requires C, 68.6; H, 5.1%).

The above neutral ethereal solution was dried (Na_2SO_4) and the solvent removed. The pale yellow oily residue furnished 2-methylcoumarone (1.5 g.) on distillation (b.p. $191^{\circ}/760$ mm). The high boiling residue in the distilling flask was dissolved in acetic acid (5 c.c.) and left overnight when a solid separated (ca. 1 g.). This crystallised from benzene-petroleum ether in colorless prisms, m.p. $168-69^{\circ}$. The compound gave a violet-red colour with H_2SO_4 and appeared to be a polymeride of 2-methylcoumarone. [Found: C, 81.1; H, 7.1; O, 6.2. $(\text{C}_9\text{H}_6\text{O})_n$ requires C, 81.8; H, 6.1%].

(b) A mixture of 3-acetylcoumarone-2 (0.5 g.), acetic acid (6 c.c.) and HCl (4 c.c.) was boiled for 8 hours. The colorless solution was poured into water and the crystalline product collected and crystallised from aqueous alcohol in colorless plates, m.p. $191-92^{\circ}$, showing a negative ferric reaction. (Found: C, 68.4; H, 4.6. Calc. for $\text{C}_{11}\text{H}_8\text{O}_5$: C, 68.2; H, 4.5%).

2-Ethylcoumarone-3-carboxylic acid was similarly prepared as above from 3-propionylcoumaranone-2. The acid crystallised from aqueous alcohol in colorless needles, m.p. 115°. (Found: C, 69.8; H, 5.1. $C_{11}H_{10}O_3$ requires C, 69.5; H, 5.3%.)

6-Methoxy-2-methylcoumarone-3-carboxylic acid was similarly prepared with the aid of HCl from (XII: R=Me; R'=COMe) (preparation given below). The acid crystallised from aqueous alcohol in pinkish plates, m.p. 106°. (Found: C, 63.8; H, 4.9. $C_{11}H_{10}O_4$ requires C, 64.1; H, 4.8%.)

2-Phenylcoumarone was obtained by boiling 3-benzoylcoumaranone-2 with HCl in acetic acid for 8 hours. The compound crystallised from alcohol in colorless plates, m.p. and mixed m.p. 120°.

6-Methoxyisocoumaranone (X).—The azlactone (10 g., m.p. 150°), derived from 2-hydroxy-4-methoxybenzaldehyde (Robertson, *loc. cit.*), was hydrolysed by refluxing for 24 hours with a mixture of hydrated barium hydroxide (45 g.), alcohol (45 c.c.) and water (200 c.c.). The barium salt was collected, washed with water and decomposed with hydrochloric acid. *2-Hydroxy-4-methoxyphenylpyruvic acid* was obtained which crystallised from acetic acid in small prisms, m.p. 154-55° (gas evolution), developing a bluish colour with ferric chloride. (Found: C, 57.2; H, 4.8. $C_{11}H_{10}O_5$ requires C, 57.1; H, 4.8%). If the above hydrolysis is done for 8 hours and the barium salt worked up, a mixture of the above α -ketonic acid and the α -lactonic acid is obtained; the latter crystallises from aqueous acetic acid in colorless prisms, m.p. 217° (rothing). The compound showed no ferric reaction. (Found: C, 64.5; H, 5.1. $C_{11}H_{10}O_5N$ requires C, 65.2; H, 4.8%). When NaOH is employed in place of baryta, the isolation of the products becomes very difficult (cf. Jatzkewitz and Offe, *Chem. Ber.*, 1947, 80, 474).

The ketonic acid (12.0 g.) was dissolved in aqueous NaOH (100 c.c., 10%) and treated at 0°-5° with hydrogen peroxide (15 c.c., 30%). The mixture was left overnight, acidified with HCl and extracted with ether (4 \times 30 c.c.). *2-Hydroxy-4-methoxyphenylacetic acid* was obtained on removal of the ether (yield, 5.5 g.). This crystallised from alcohol-benzene as cream-coloured prisms, m.p. 130° (lit., m.p. 130°).

The acid (5.0 g.) was fractionated in vacuum when the colorless distillate (3.3 g.) immediately solidified, furnishing 6-methoxyisocoumaranone; m.p. 55-56°. (Found: C, 65.5; H, 4.8. Calc. for $C_{11}H_{10}O_2$: C, 65.8; H, 4.9%). Frometka (*loc. cit.*) records m.p. 56°.

Self-condensation of 6-Methoxyisocoumaranone.—A solution of the isocoumaranone (1.6 g.) in benzene (10 c.c.) was added to a suspension of sodium hydride (0.26 g.) in benzene (5 c.c.) and the mixture refluxed for 6 hours. The sodium salt of the self-condensation product began to separate after 1 hour. The mixture was then cooled and carefully decomposed with water and the aqueous layer acidified to furnish 3-(2-hydroxy-4-methoxyphenylacetyl)-6-methoxycoumaranone-2 (1.1 g.). The compound showed a bluish green ferric reaction and crystallised from acetic acid in thick plates, m.p. 160°. (Found: C, 65.5; H, 4.7. $C_{12}H_{10}O_4$ requires C, 65.8; H, 4.9%). The compound was soluble in sodium bicarbonate and developed a deep blue coloration with H_2SO_4 . *U.V. absorption*: λ_{max}^{NaOH} 3500 Å (log ϵ , 3.63), 3135 Å (log ϵ , 4.27). *Infra-red spectrum*: λ_{OH}^{NaOH} 3.25 (OH phenolic), 3.45 (OH hydrogen bonded), 5.80s (lactone carbonyl), 6.07s, 6.14s (double bond), 8.9.0s (ether)p.

The diacetyl derivative was obtained by boiling the compound with acetic anhydride for 1½ hours. It crystallised from alcohol in drab needles, m.p. 162-63°. (Found: C, 64.6; H, 4.8. $C_{12}H_{10}O_6$ requires C, 64.1; H, 4.8%). The compound showed no ferric reaction and was insoluble in cold dilute alkali.

6-Methoxy-3-acetylcoumaranone-2.—6-Methoxyisocoumaranone or its self-condensation product (0.5 g.) was refluxed with acetic anhydride (6 c.c.) and sodium acetate (0.3 g.) for 1½ hours and the mixture poured into water. The enolic acetyl derivative of 6-methoxy-3-acetylcoumaranone-2 (0.5 g.) was obtained which crystallised from acetic acid in slightly brownish needles, m.p. 143°, insoluble in sodium bicarbonate. (Found: C, 62.8; H, 5.0. $C_{11}H_{10}O_5$ requires C, 62.0; H, 4.8%). This acetyl derivative was shaken for 2½ hours with an excess of sodium carbonate solution (15%) at 60°. The aqueous solution was clarified with charcoal and acidified. The brown precipitate of 6-methoxy-3-acetylcoumaranone-2 crystallised from acetic acid in cream-coloured prisms, m.p. 148°, exhibiting a deep blue ferric reaction. (Found: C, 64.2; H, 5.0. $C_{11}H_{10}O_5$ requires C, 64.1; H, 4.9%). *U. V. absorption:* λ_{max}^{NaOH} 3400 Å (log ϵ , 3.92).

Propionyl Derivative of 6-Methoxy-3-propionylcoumaranone-2.—A mixture of 6-methoxyisocoumaranone (0.3 g.), propionic anhydride (1 c.c.) and sodium propionate (0.1 g.) was heated on the water-bath for 2 hours and then poured into a cooled potassium carbonate solution. The crystalline product (0.2 g.) crystallised from alcohol in brownish plates, m.p. 74-75°. (Found: C, 65.5; H, 5.7. $C_{12}H_{14}O_5$ requires C, 65.2; H, 5.8%).

6-Methoxy-3-benzoylcoumaranone-2.—A mixture of 6-methoxyisocoumaranone (0.35 g.), benzoic anhydride (1.4 g.) and sodium benzoate (0.5 g.) was heated at 175° for 2 hours and then water was added to the cooled mixture. Benzene (5 c.c.) and aqueous sodium carbonate solution (10 c.c., 10%) were added to the mixture and shaken mechanically for 3 hours at 45°. The aqueous layer was removed, acidified and the mixture warmed till benzoic acid just dissolved, and the crystalline residue filtered quickly. 6-Methoxy-3-benzoylcoumaranone-2 (0.35 g.) was crystallised from methanol and obtained in yellowish needles, m.p. 116°. The compound showed a deep blue ferric reaction. (Found: C, 71.7; H, 4.4. $C_{15}H_{14}O_5$ requires C, 71.6; H, 4.5%). *U. V. absorption:* λ_{max}^{NaOH} 3450 Å (log ϵ , 3.98).

Isomerization of the Self-condensation Product.—The above mentioned self-condensation product of 6-methoxyisocoumaranone (0.3 g.) was dissolved in acetic acid (5 c.c.) and boiled with HCl (1.5 c.c.) for 3 hours and then poured into water. 6-Methoxy-2-(2-hydroxy-4-methoxybenzyl)-coumarone-3-carboxylic acid (I; R=H; R'=OMe) (1.0 g.) was obtained as a gum which soon solidified. The compound separated from acetic acid in brownish needles, m.p. 190-92°. (Found: C, 65.2; H, 4.8. $C_{15}H_{14}O_6$ requires C, 65.0; H, 4.9%). The compound showed a pink colour with H_2SO_4 .

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